Chemical and Biological Thermodynamics: Principles to Applications
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Lecture - 12
Discussion on Gibbs Energy

Let us discuss about Gibbs energy today, which is also called free energy. The reason for the word free we have discussed in the previous lecture. Gibbs energy and the corresponding changes in Gibbs energy when a process takes place at constant temperature and pressure it is very important to understand, because the change in Gibbs free energy at constant temperature and pressure, if it is less than zero then the process is spontaneous. That is one of the criteria of spontaneity that we discussed in the previous lecture.

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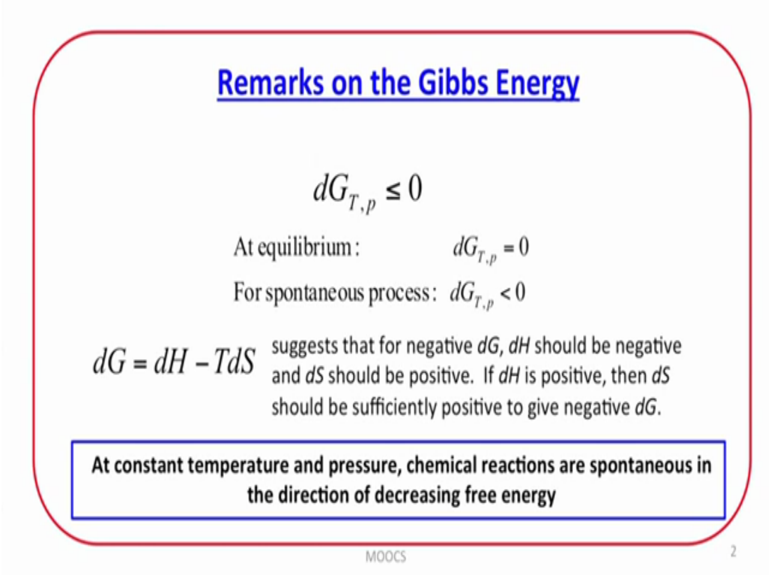

Remarks on the Gibbs Energy

$$dG_{T,p} \le 0$$

At equilibrium: $dG_{T,p} = 0$

For spontaneous process: $dG_{T,p} < 0$

$dG = dH - TdS$ suggests that for negative *dG*, *dH* should be negative and *dS* should be positive. If *dH* is positive, then *dS* should be sufficiently positive to give negative *dG*.

At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing free energy

Let us now discuss some remarks on the Gibbs energy. The change in Gibbs free energy or Gibbs energy at constant temperature and pressure should be less than or equal to 0 that is the criteria of spontaneity. And as we discussed in the previous lecture that if the process is reversible or if the process is at equilibrium then there is no change in Gibbs free energy dG at constant temperature and pressure is equal to 0. However, for the spontaneity, the change in Gibbs free energy should be negative. This is the most widely used criteria of spontaneity, because it is easy to maintain temperature and pressure constant rather than maintaining temperature and volume constant. So, that is why most of the time when we say that for spontaneity of the process let us take a look at the change in Gibbs free energy of the reaction. And if the change in Gibbs free energy of the reaction at constant temperature and pressure is less than 0, then the reaction is spontaneous in that direction.

For a small change dG is equal to dH minus T dS, so obviously here dG for dG to be negative that will be supported by negative value of dH and a positive value of dS. However, even if the reaction turns out to be endothermic, if dH is positive then there has to be sufficient increase in the entropy of the system that is dS should be sufficiently positive, so that minus T dS overcomes dH to give a negative value of dG. Therefore, let us make this comment that at constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing free energy.

In the previous lecture, we showed that the maximum work available from a system is equal to change in the Helmholtz free energy, and that maximum work was inclusive of pressure, volume work, and non-pressure, volume, work. Now, if we are only interested in the non-pressure volume work, which sometimes we call as extra work or which sometimes we call as useful work and sometimes some books write as additional work whatever terminology is given, one of the example of such a work is the work of electrical or electrical work.

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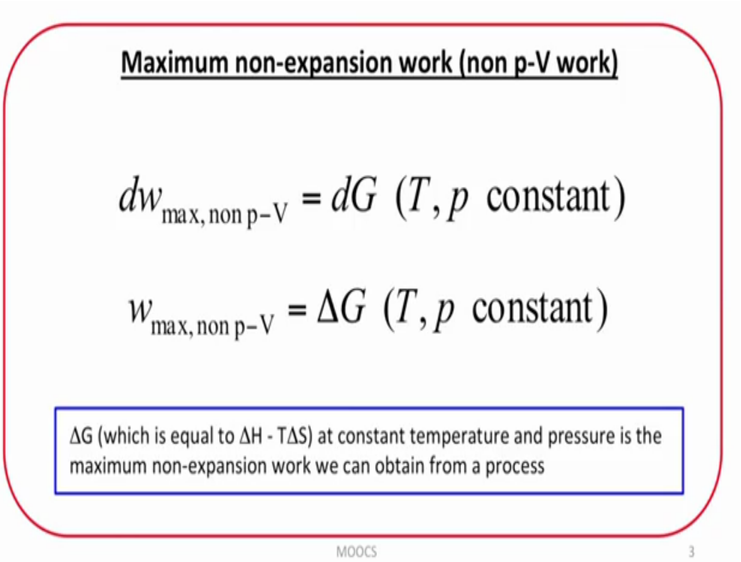

Maximum non-expansion work (non p-V work)

$$dw_{\text{max, non p-V}} = dG \ (T, p \ \text{constant})$$

$$w_{\text{max, non p-V}} = \Delta G \ (T, p \ \text{constant})$$

ΔG (which is equal to ΔH - TΔS) at constant temperature and pressure is the maximum non-expansion work we can obtain from a process

The maximum non-expansion work or non-pressure, volume, work can be calculated from the change in Gibbs free energy at constant temperature and pressure. And for a finite change w max is given by delta G. So, now our goal is to prove that w max as seen in the slide that the maximum work non-pressure, volume, work obtainable from the system is equal to delta G at constant temperature and pressure.

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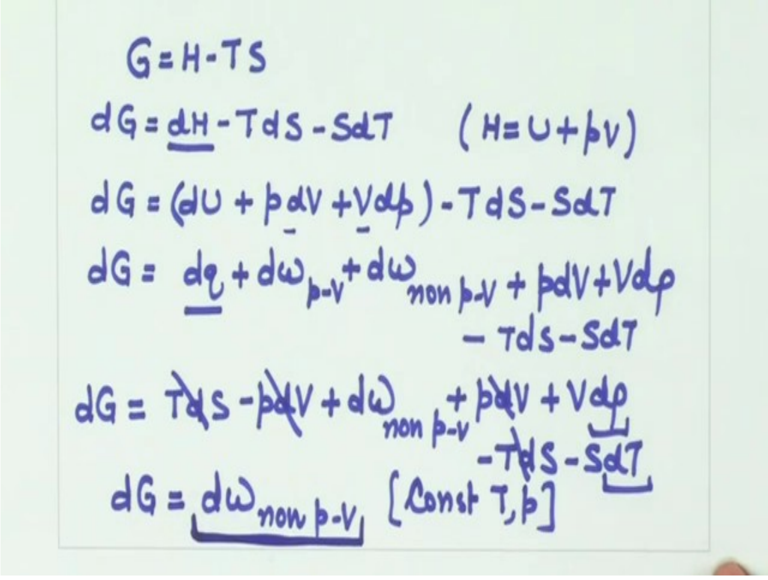

$$G = H - TS$$

$$dG = \underline{dH} - TdS - SdT \qquad (H = U + pV)$$

$$dG = (dU + \underline{p}\,dV + \underline{V}dp) - TdS - SdT$$

$$dG = \underline{dq} + d\omega_{p-V} + d\omega_{non\ p-V} + pdV + Vdp - TdS - SdT$$

$$dG = \cancel{TdS} - \cancel{pdV} + d\omega_{non\ p-V} + \cancel{pdV} + \underbrace{Vdp} - \cancel{TdS} - \underbrace{SdT}$$

$$dG = \underline{d\omega_{non\ p-V}} \quad [\text{Const } T, p]$$

For this, I will start with the definition of Gibbs free energy G is equal to H minus T S. Now, let there be some advancement in the reaction or the process. So, dG is equal to dH minus T dS minus S dT. Now, I will use H is equal to U plus p v. And I will substitute for dH. So, dG is equal to dH, I will take derivative of this dU plus p dV plus V d p, this is for dH and remaining I will write minus T dS minus S dT. Let us further continue. Now, I will use the first law dU is equal to dq plus dw, this is dU. Now, this dw now I am making some change over here, this is pressure, volume, work plus dw. Let me write as non-pressure, volume, work which you can write as dw extra or there are various terminologies which can be used.

This entire thing d this d this is for dU, dU is equal to dq plus dw now instead of d w, I have now divided this dw into pressure volume and non-pressure, volume. Now, the remaining terms are still there plus p dV plus V dp minus T dS minus S dT. Now, let us see what shape it takes dG is equal to dq if the process is reversible you know that dq reversible is equal to T dS. And dw let us invoke reversibility condition is minus p dV that we have discussed. And let me retain this as non p-v, then I have plus p dV plus V dp minus T dS minus S d T, T dS, T dS goes, p dV, p dV goes. Now, if I maintain the pressure and temperature constant then dp and dT will also become 0. So, therefore, dG becomes equal to d w non-pressure volume. What are the constraints constant temperature, and pressure.

Now, since we substituted d q reversible is equal to T dS, and d w reversible equal to minus p d v since we have used reversible conditions therefore, the work obtained must be maximum. We have already established that you can draw maximum work from a system when it is operating under reversible conditions. So, therefore, this work has to be maximum because the system is operating under reversible conditions. So, thus let us go back to the slide we have proved that d w maximum non-pressure volume is equal to change in Gibbs free energy at constant temperature and pressure.

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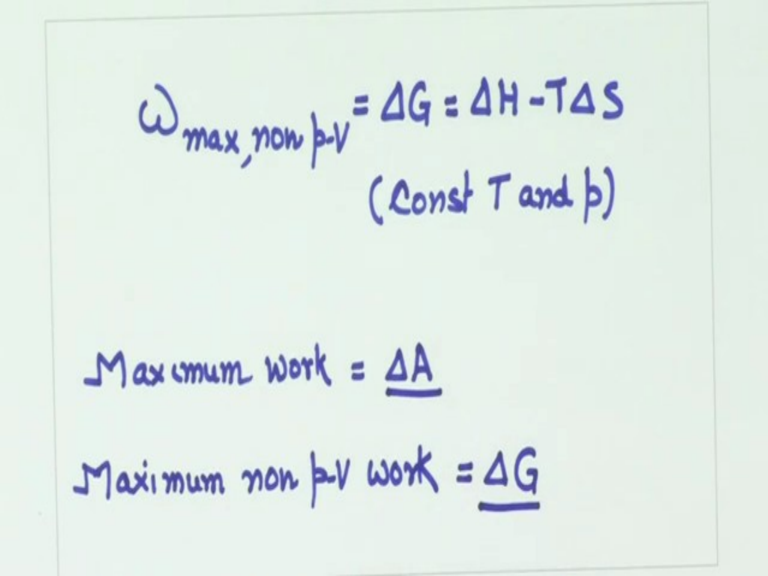

$w_{max,\, non\ p\text{-}V} = \Delta G = \Delta H - T\Delta S$

(Const T and p)

Maximum work = $\underline{\Delta A}$

Maximum non p-V work = $\underline{\Delta G}$

And for a finite change, W max, non p-v is equal to delta G at constant temperature and pressure which is equal to delta H minus T delta S. And of course, our constraints still are there constant temperature and pressure, and this is what we wanted to prove. So, let us take a look at this comment. Now, delta G, which is equal to delta H minus T delta S at constant temperature and pressure is the maximum non-expansion work we can obtain from a process, so the points to be remembered that if we are interested in knowing the maximum work, just maximum work, we have to act upon A, we need to know delta A.

And if we are interested in knowing maximum non pressure volume work, this is given by delta G, of course, this is at constant temperature, this is at constant temperature and pressure, let us not forget the constants.

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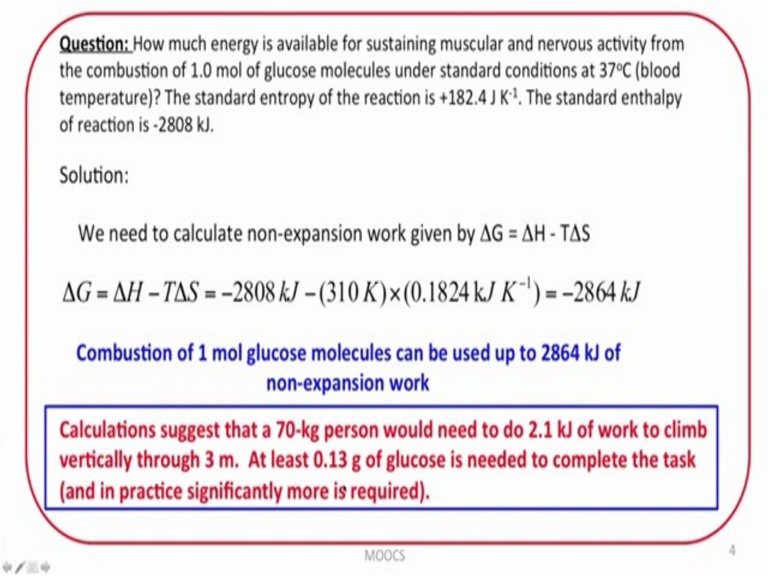

Question: How much energy is available for sustaining muscular and nervous activity from the combustion of 1.0 mol of glucose molecules under standard conditions at 37°C (blood temperature)? The standard entropy of the reaction is +182.4 J K^{-1}. The standard enthalpy of reaction is -2808 kJ.

Solution:

We need to calculate non-expansion work given by $\Delta G = \Delta H - T\Delta S$

$$\Delta G = \Delta H - T\Delta S = -2808\,kJ - (310\,K)\times(0.1824\,kJ\,K^{-1}) = -2864\,kJ$$

Combustion of 1 mol glucose molecules can be used up to 2864 kJ of non-expansion work

Calculations suggest that a 70-kg person would need to do 2.1 kJ of work to climb vertically through 3 m. At least 0.13 g of glucose is needed to complete the task (and in practice significantly more is required).

MOOCS

Let us take an example which will further clarify the meaning of this the question is how much energy is available for sustaining muscular and nervous activity from the combustion of 1 mol of glucose molecules under standard conditions at 37 degree Celsius, 37 degree Celsius is blood temperature. The standard entropy of the reaction is plus 182.4 joules per Kelvin and the standard enthalpy of reaction is minus 2808 kilojoules. What we need to know how much energy is available for sustaining muscular and nervous activity that means, how much work which is non pressure volume work, it is not a pressure volume work it is non-pressure volume work, which we need to calculate because that is the work required for sustaining muscular and nervous activity.

The equation to be used for calculating delta G will be equal to delta H minus T delta S and the numbers are given delta H is given minus 2808 kilojoules. Temperature is given, delta S is given, so you put the values of temperature and delta S in appropriate units, what you see here is the maximum non pressure volume work which you can get is minus 2864 kilojoules. So, this is how you calculate the maximum non pressure volume work. So, that means, now if you write down a chemical reaction corresponding to combustion of 1 mol of glucose molecules, and then do these calculations, it turns out that the combustion of 1 mol glucose molecules can be used up to 2864 kilojoules of non expansion work this is the amount of work that can be obtained just by the combustion of one mol of glucose molecules.

Let us now look at the next comment suppose a 70 kilogram person needs to climb up vertically through 3 meter just vertically. You can do the calculations; you will find out that a 70 kilogram person would need to do 2.1 kilojoules of work to climb vertically through 3 meter. And then if you convert this energy in terms of number of moles of glucose required or number of moles can then be converted into amount of glucose or grams of glucose required. What you need is the calculation suggest that you need 130 milligram or 0.13 gram of glucose to complete the task that is if the person has to vertically climb up by 3 meter. And actually when you go up the hill, you just cannot go vertically up you have to take a round or than alternate path one has to take. So, therefore, in practice significantly more energy is required. So, significantly more amount of glucose is required. So, I hope that it is very clearly noted that whenever we want to calculate the non pressure volume work, which is sometimes called extra work, additional work, useful work various terminologies have been used we need to act upon delta G.

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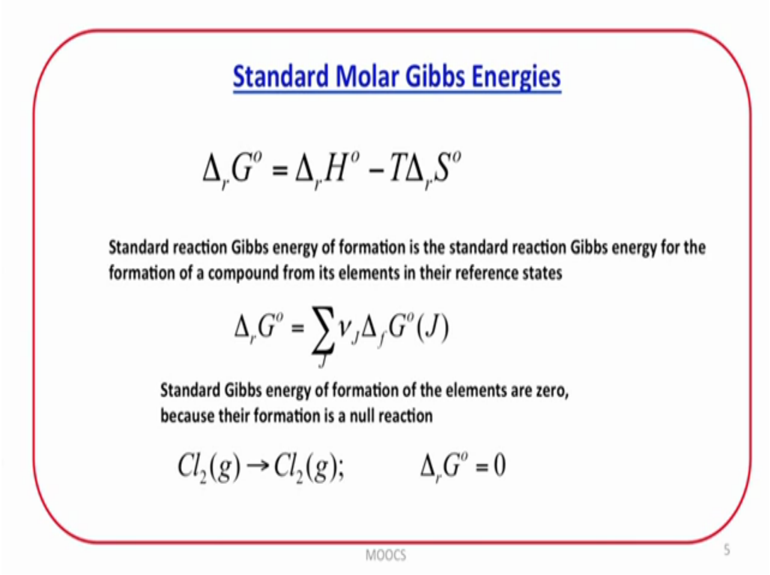

Standard Molar Gibbs Energies

$$\Delta_r G^o = \Delta_r H^o - T\Delta_r S^o$$

Standard reaction Gibbs energy of formation is the standard reaction Gibbs energy for the formation of a compound from its elements in their reference states

$$\Delta_r G^o = \sum_J \nu_J \Delta_f G^o(J)$$

Standard Gibbs energy of formation of the elements are zero, because their formation is a null reaction

$$Cl_2(g) \rightarrow Cl_2(g); \qquad \Delta_r G^o = 0$$

How do you get delta G, Standard molar Gibbs energies. Standard state we have already discussed, what is the standard state. And we also know the relation between delta G delta H and T delta S, this is the relation. Delta G naught is equal to delta H naught minus T delta S naught r, here represents reaction this is for the reactions. How do we get the values of delta Gs, but let us first of all look at the definition of standard reaction Gibbs free energies of formation.

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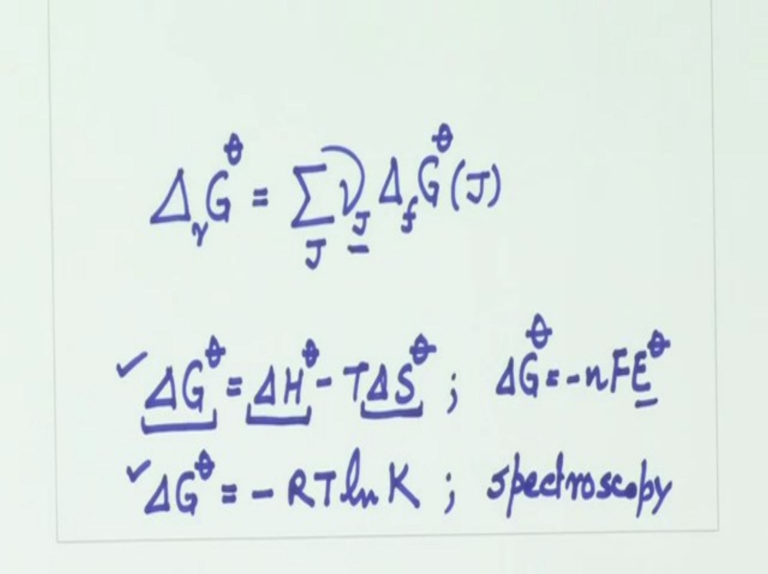

$$\Delta_r G^\ominus = \sum_J \underline{\nu_J}\, \Delta_f G^\ominus(J)$$

✓ $\underline{\Delta G^\ominus} = \underline{\Delta H^\ominus} - T\underline{\Delta S^\ominus}$; $\Delta G^\ominus = -nF\underline{E}^\ominus$

✓ $\Delta G^\ominus = -RT\ln K$; spectroscopy

The standard reaction Gibbs free energies of a reaction can be calculated from this expression J nu J delta formation G naught of species J. Once again, here this Stoichiometric number is positive for products and negative for reactants. So, if we know the information on free energies of formation, we can calculate the free energy of reaction. For the definition of free energy of formation, let us go back to the slide. The standard reaction Gibbs energy of formation is the standard reaction Gibbs energy for the formation of a compound from its elements in their reference states. This is the overall equation that is to be used to calculate the reaction Gibbs free energies. Also please note that the standard Gibbs energy of formation of the elements are 0, because these are the formation of a null reaction.

Let us take an example say I want to know what is the value of standard Gibbs free energy of formation of chlorine gas. The reference state for chlorine gas is chlorine gas itself. Therefore, the overall reaction is chlorine gas going to chlorine gas and obviously, for such type of reaction the reaction Gibbs free energies have to be equal to 0.

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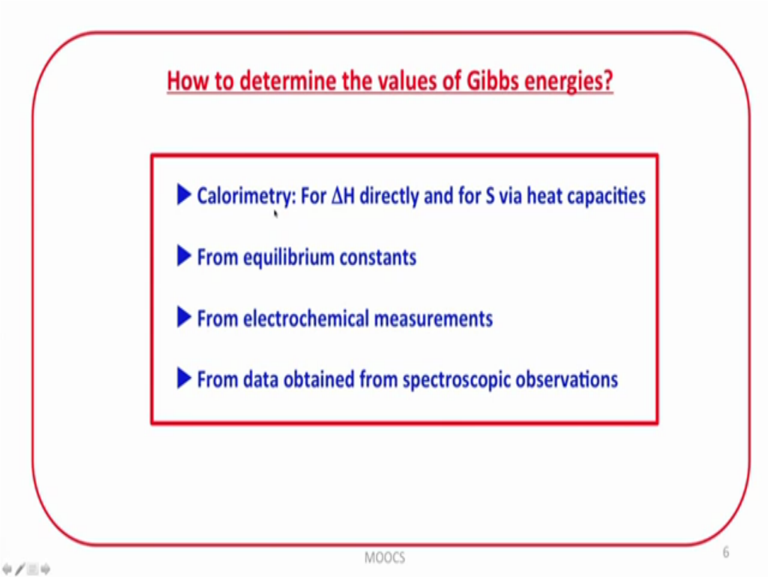

How to determine the values of Gibbs energies?

- Calorimetry: For ΔH directly and for S via heat capacities
- From equilibrium constants
- From electrochemical measurements
- From data obtained from spectroscopic observations

So, now naturally the another question can come to mind is how to determine the values of Gibbs energy. Experimentally, how do we determine the values of Gibbs energy. First is calorimetry, because we know that delta G naught is equal to delta H naught minus T delta S naught. So, change in Gibbs free energy we can very, very easily determine if we have the information on enthalpy of the reaction and also change in entropy. Both delta H and delta S can be determined by calorimetry. Delta H can be determined if we know how much heat has been supplied at constant pressure, and the entropies means you have to have the information on heat capacities.

The second method is from equilibrium constant. This we will discuss later delta G naught I can put R or omit R, you keep it in mind that this is for a reaction is minus R T log k, this we will prove later. So, this we said that by from calorimetry and if we know the value of equilibrium constant, we can get the value of delta G naught. It is a different matter now how to calculate the value of how to determine the value of equilibrium constant. Several methods can be used. And actually we can discuss about the methods at some in a different lecture.

Third one is from electrochemical measurements. We know delta G naught is equal to minus n F E naught. So, if I know the potential cell potential or potential corresponding to the particular reaction, which involves the change of electrons delta G naught can be measured from electrochemical measurements. And the fourth one is from spectroscopy.

In statistical thermodynamics, we talk about partition functions and the information on partition function comes from spectroscopic observations.

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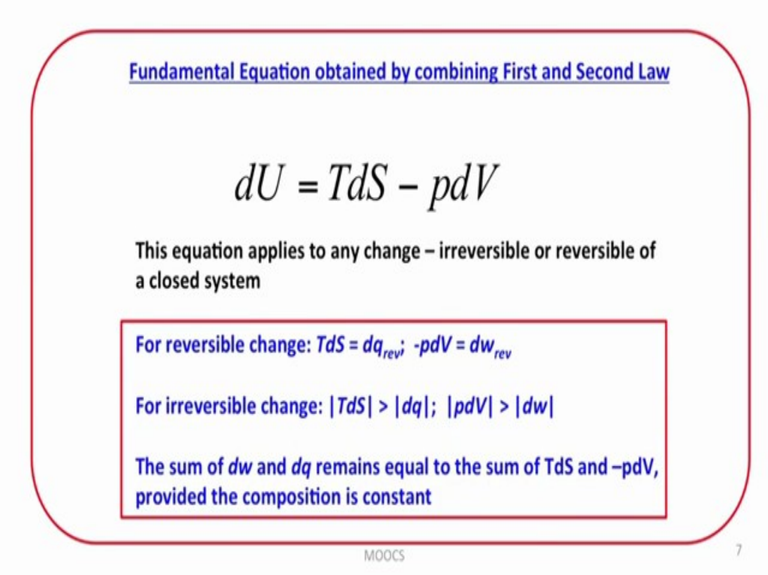

Fundamental Equation obtained by combining First and Second Law

$$dU = TdS - pdV$$

This equation applies to any change – irreversible or reversible of a closed system

For reversible change: $TdS = dq_{rev}$; $-pdV = dw_{rev}$

For irreversible change: $|TdS| > |dq|$; $|pdV| > |dw|$

The sum of dw and dq remains equal to the sum of TdS and –pdV, provided the composition is constant

Now, let us move towards more information from the first and second law from first law we discussed d u is equal to d q plus d w.

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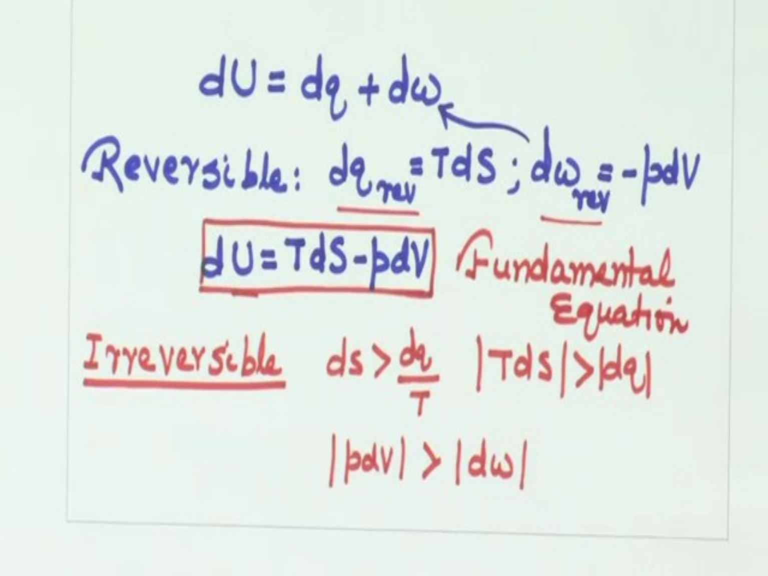

$$dU = dq + dw$$

Reversible: $dq_{rev} = TdS$; $dw_{rev} = -pdV$

$\boxed{dU = TdS - pdV}$ Fundamental Equation

Irreversible $ds > \frac{dq}{T}$ $|Tds| > |dq|$

$|pdV| > |dw|$

And let us say if the process is reversible then dq reversible is equal to T dS; and dw reversible is equal to minus p dV. And if I substitute this over here what I get is dU is equal to T dS minus p dV. Please note that we have used the reversible conditions and come up with this equation. Now, the question is this equation applicable to reversible changes, or both reversible and irreversible changes? The point to be noted in this equation is that on the left hand side, you have U, U is a state property. Therefore, the value of dU is going to be same whether the process is reversible or the process is irreversible as long as the initial and final states are same. So, how this can be used for both reversible and irreversible processes how it is applicable to both reversible and irreversible processes.

Now, suppose if the process is irreversible, then from Clausius inequality dS is greater than or equal to dq by T that means, T dS is greater than dq. And let me just take the mod and the mod of p dV will also be greater than dw, because reversible work when we talk about reversible work we talk about p dV minus p dV, I am taking mod over here, so that will be more than the work done in an irreversible process. So, T dS is greater than dq T dS is greater than dq and p dV is also greater than dw their mods. So, whatever is increasing here the same is increasing here, so that the difference remains same. So, T dS minus p dV remains same when the process is reversible or irreversible.

Therefore, this is applicable to both reversible and irreversible changes, and this is called fundamental equations. And that is what is described in this slide that dU is equal to T dS minus p dV that is what we discussed. And this equation applies to any change whether it is irreversible or reversible of a closed system. You see we are not talking about an open system composition is not changing. And here once again the same explanation is given over here that this T dS minus p dV will remain same, whether the process is reversible or irreversible and that is why the name is given fundamental equation this name is given to this equation.

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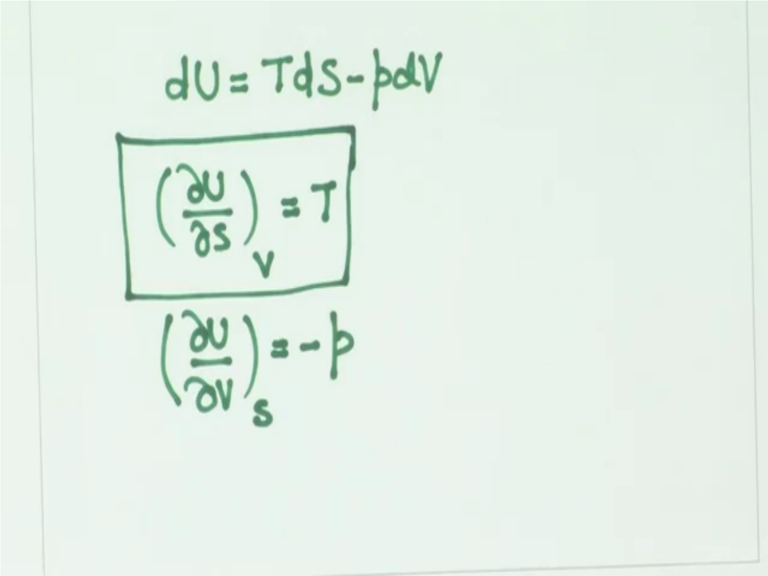

$$dU = TdS - pdV$$

$$\boxed{\left(\frac{\partial U}{\partial S}\right)_V = T}$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -p$$

Now, from fundamental equation, we can get some more thermodynamic quantities. dU is equal to T dS minus p dV that is what we discussed. From this equation, I can write dou U by dou S at constant volume is equal to T and dou U by dou V at constant entropy is equal to minus p. If I fix the volume dV is 0, so dou U by dou S, since I am fixing volume, I have take partial derivative is T and same way you fix the entropy then d U by dV at constant entropy is equal to minus p. Note that this is the pure thermodynamic definition of temperature which is the change in internal energy with respect to change in entropy at constant work. So, by coming up with these kind of equations, we are slowly and slowly unfolding the power of thermodynamics. These kind of relations will allow us to connect one thermodynamic quantity with an another thermodynamic quantities without doing the experiment and that is what is the power of these kind of equation and that is what is the power of thermodynamics.

There are few more equations, which are called Maxwell relations which further demonstrate the power of thermodynamics and that we will discuss in the next lecture. So, in today’s lecture, we discussed about the maximum non pressure, volume, work or which you call as maximum extra work or maximum useful work, whatever terminology you want to use which is equal to the change in Gibbs free energy at constant temperature and pressure. So, therefore, we should be very, very clear that which thermodynamic quantity to be used when you want to calculate the maximum work or maximum non pressure volume work.

Thank you very much.